

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C11D 3/386	A1	(11) International Publication Number: WO 97/31090 (43) International Publication Date: 28 August 1997 (28.08.97)
(21) International Application Number: PCT/US96/02229 (22) International Filing Date: 20 February 1996 (20.02.96) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HERBOTS, Ivan, Maurice, Alfons, Jan [BE/BE]; Hollegat 11, B-9230 Wetteren (BE). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B-1840 Londerzeel (BE). VAN LEEUWEN, Petrus, Johannes [BE/GB]; 4 The Warings Kelswick Drive, Nelson, Lancashire BB9 0XF (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: BR, CA, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: A CLEANING COMPOSITION COMPRISING PEROXIDASE (57) Abstract The present invention relates to a cleaning composition comprising peroxidase, an enhancer and a source of hydrogen peroxide. Said peroxidase is incorporated into a release agent, whereby said release agent is such that the level of active peroxidase is substantially held constant in the wash environment during a substantial period of the wash cycle. The cleaning composition according to the present invention achieves an improved dye transfer inhibition and/or bleaching benefits.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

A CLEANING COMPOSITION COMPRISING PEROXIDASE

Field of the invention

The present invention relates to a variety of cleaning compositions comprising peroxidase, an enhancer and a source of hydrogen peroxide.

Background of the invention

In the following, "to catalyze" means to accelerate a reaction without being consumed. Whereas, "to hydrolyze" means to break down a compound into two or more simpler compounds with the uptake of the H and OH parts of a water molecule on either side of the chemical bond cleaved.

Enzymes make up the largest class of naturally occurring proteins. Each class of enzyme generally catalyzes a different kind of chemical reaction. A class of enzymes, called peroxidase, are known for their ability as a bleaching agent and as a dye transfer inhibiting agent. These abilities of peroxidase are especially apparent in combination with an oxidisable substrate other than the dye, hereinafter called "enhancer", and a source of hydrogen peroxide. The "dye transfer inhibition" is the process comprising inhibition of the transfer of dye from a dyed substrate to

another substrate during washing of said substrates, as described for example in WO 91/05839 for fabrics.

Unfortunately, the efficacy level of said peroxidase in their natural environment, frequently does not translate into the relatively unnatural wash environment. Specifically, peroxidase characteristics such as thermal stability, pH stability, oxidative stability and substrate specificity are not necessarily optimized for utilization outside the natural environment of the enzyme.

The amino acid sequence of the peroxidase enzyme to a great extent determines the characteristics of said peroxidase. A change of the amino acid sequence of the peroxidase may alter the properties of the enzyme to varying degrees, or may even inactivate the enzyme, depending upon the location, nature and/or magnitude of the change in the amino acid sequence. In WO 95/10602, for example, an approach has been taken to alter the amino acid sequence of peroxidases in an attempt to improve their properties, with the goal of increasing the efficacy of said peroxidase for cleaning purposes as in the wash environment. Nevertheless, it is known that said peroxidase is active in the wash environment only over a limited period of time. In practice, said peroxidase remains active only over few minutes from the moment said peroxidase is released into the wash environment.

In the co-pending International patent application No. PCT/DK95/00214 a dye transfer inhibitory preparation comprising granules containing co-granulated peroxidase and enhancer is described. Said granules are coated with a slow-release coating. In this manner, the total amount of peroxidase in a cleaning composition is slowly and gradually released in the wash environment. But the corresponding activity level of the peroxidase in the wash environment also increases slowly during the wash cycle. Indeed, the maximum activity level of this slow released peroxidase is reached only very late from the start of the wash cycle. For example, under certain wash environment conditions the maximum activity level of said slow released peroxidase is reached after about 20 minutes. This means that the maximum efficacy of said peroxidase as a bleaching and a dye transfer inhibiting agent is reached relatively late from the start of the wash cycle. Furthermore, the maximum activity level of this slow released peroxidase

immediately decreases in the wash environment after having reached the maximum activity level.

It is therefore an object of the present invention to provide a cleaning composition comprising peroxidase whose effective activity level for dye transfer inhibition and bleaching is maintained for a relatively long period of time of the wash cycle.

Summary of the invention

The present invention is a cleaning composition comprising peroxidase, an enhancer and a source of hydrogen peroxide. Said peroxidase is incorporated into a release agent. Said release agent is such that the level of active peroxidase is substantially held constant in the wash environment during a substantial period of the wash cycle.

Detailed description of the invention

In the following, the "wash environment" is a liquid environment determined by certain wash conditions. Wash conditions may be hardness and temperature of water. The surfactant system dissolved in the water, which may also determine the pH of the wash environment, may be another possible parameter of the wash condition. Our "standard" wash environment is a wash environment having a water hardness of 12 °dH, pH 10.0 and a temperature of 35 °C.

The cleaning composition according to the present invention comprises peroxidase, an enhancer and a source of hydrogen peroxide.

Peroxidases

Peroxidase enzymes (EC 1.11.1) employed in the context of the invention may very suitably be, e.g., any peroxidase comprised by the enzyme classification EC 1.11.1.7; peroxidase fragments, exhibiting peroxidase activity, as well as synthetic or semi-synthetic peroxidase

derivatives [e.g. with porphyrin ring systems], or microperoxidases (see, e.g., US 4,077,768, EP 0 537 381, WO 91/05858 and WO 92/16634)] are also relevant in the context of the invention. Suitable peroxidases are known from microbial, plant and animal origins. Other possible peroxidase enzymes may be derived with protein engineering methods where one or several amino acids of the natural peroxidase enzyme may have been replaced by other amino acids.

Preferably, the peroxidase employed in the method of the present invention may be produced by plants (e.g. horseradish or soy bean peroxidase) or micro-organisms such as fungi or bacteria. Some preferred fungi include strains belonging to the subdivision Deuteromycotina, class Hyphomycetes, e.g. *Fusarium*, *Humicola*, *Tricoderma*, *Myrothecium*, *Verticillium*, *Arthromyces*, *Caldariomyces*, *Ulocladium*, *Embellisia*, *Cladosporium* or *Dreschlera*, in particular *Fusarium oxysporum* (DSM 2672), *Humicola insolens*, *Trichoderma reesei*, *Myrothecium verrucaria* (IFO 6113), *Verticillium albo-atrum*, *Verticillium dahliae*, *Arthromyces ramosus* (FERM P-7754), *Caldariomyces fumago*, *Ulocladium chartarum*, *Embellisia alli* or *Dreschlera halodes*.

Other preferred fungi include strains belonging to the subdivision Basidiomycotina, class Basidiomycetes, e.g. *Coprinus*, *Phanerochaete*, *Coriolus* or *Trametes*, in particular *Coprinus cinereus* f. *microsporus* (IFO 8371), *Coprinus macrorhizus*, *Phanerochaete chrysosporium* (e.g. NA-12) or *Trametes* (previously called *Polyporus*), e.g. *T. versicolor* (e.g. PR428-A). Further preferred fungi include strains belonging to the subdivision Zygomycotina, class Mycoraceae, e.g. *Rhizopus* or *Mucor*, in particular *Mucor hiemalis*.

Some preferred bacteria include strains of the order Actinomycetales, e.g. *Streptomyces spheroides* (ATCC 23965), *Streptomyces thermoviolaceus* (IFO 12382) or *Streptoverticillium verticillium* ssp. *verticillium*. Other preferred bacteria include *Bacillus pumilus* (ATCC 12905), *Bacillus stearothermophilus*, *Rhodobactersphaeroides*, *Rhodomonas palustri*, *Streptococcus lactis*, *Pseudomonas putrefaciens* (ATCC 15958) or *Pseudomonas fluorescens* (NRRL B-11). Further preferred bacteria include strains belonging to *Myxococcus*, e.g. *M. virescens*.

Other relevant peroxidases are "haloperoxidases" (see, e.g., US 4,937,192), such as chloride peroxidases (EC 1.11.1.10), bromide peroxidases, and iodide peroxidases (EC 1.11.1.8). Other potential sources of useful peroxidases are listed in B.C. Saunders et al., *Peroxidase*, London, 1964, pp. 41-43.

The peroxidase may furthermore be one which may be produced by a method comprising cultivating a host cell transformed with a recombinant DNA vector which carries a DNA sequence encoding said peroxidase as well as DNA sequences encoding functions permitting the expression of the DNA sequence encoding the peroxidase, in a culture medium under conditions permitting the expression of the peroxidase and recovering the peroxidase from the culture. Particularly, a peroxidase produced in a recombinant manner is a peroxidase derived from a *Coprinus* sp., in particular *C. macrorhizus* or *C. cinereus* according to WO 92/16634.

As already indicated to some extent above, the term peroxidase as employed in the context of the invention embraces substances possessing peroxidase activity, such as peroxidase-active fragments derived from cytochromes, hemoglobin or peroxidase enzymes, and synthetic or semi-synthetic derivatives thereof, e.g. iron porphyrins, iron porphyrins and iron phthalocyanine and derivatives thereof. The peroxidase employed in a preparation of the invention will very suitably often be a *Coprinus* peroxidase, a *Myxococcus* peroxidase, or a horseradish peroxidase.

Enhancers.

The enhancer can be any suitable peroxidase enhancer. Examples of enhancers include the following : halide ions (e.g. chloride and bromide); certain metal ions (e.g. Mn^{2+}); phenolic species (e.g. p-hydroxycinnamic acid 2,4-dichlorophenol, vanillin, 7-hydroxycoumarin, 6-hydroxy-2-naphthoic acid, and p-hydroxybenzenesulfonate); 2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonate (ABTS; see, e.g., WO 94/12620); and 10-methyl-, 10-ethyl- and 10-propyl-phenothiazine (see, e.g., WO 94/12621). Numerous other enhancers or enhancing agents are disclosed in WO 94/12619, WO 94/12620 and WO 94/12621.

Preferred enhancers in the context of the present invention are 10-phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621), and dye-transfer inhibitory co-granulate preparations of the invention comprising such enhancers have good storage stability (shelf life), and lead to very satisfactory dye-transfer inhibition in fabric washing (vide infra).

Source of hydrogen peroxide

The bleaches suitable for the present invention include sources of peroxygen bleaches. Examples of suitable sources of peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5,5-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591), or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect.

It may be also desirable to utilize an enzymatic process for hydrogen peroxide formation. Thus, the process according to the invention may additionally comprise adding an enzymatic system (i.e. an enzyme and a substrate therefor) which is capable of generating hydrogen peroxide at the beginning or during the washing.

One such category of hydrogen peroxide generating systems comprises enzymes which are able to convert molecular oxygen and an organic or inorganic substrate into hydrogen peroxide and the oxidized substrate respectively. These enzymes produce only low levels of hydrogen peroxide, but they may be employed to great advantage in the process of

the invention as the presence of peroxidase ensures an efficient utilization of the hydrogen peroxide produced.

Preferred hydrogen peroxide-generating enzymes are those which act on cheap and readily available substrates which may conveniently be included into detergent compositions. An example of such a substrate is glucose which may be utilized for hydrogen peroxide production by means of glucose oxidase. Suitable oxidases include those which act on aromatic compounds such as phenols and related substances. Other suitable oxidases are urate oxidase, galactose oxidase, alcohol oxidases, amine oxidases, amino acid oxidase, amyloglucosidase, and cholesterol oxidase.

The preferred enzymatic systems are alcohol and aldehyde oxidases. The more preferred systems for granular detergent application would have solid alcohols, e.g. glucose whose oxidation is catalysed by glucose oxidase to glucuronic acid with the formation of hydrogen peroxide. The more preferred systems for liquid detergent application would involve liquid alcohols which could also act as, for example, solvents. An example is ethanol/ethanol oxidase. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarboxylic acids.

The present invention provides a cleaning composition comprising peroxidase whose effective activity level for dye transfer inhibition and/or bleaching is maintained substantially constant for a relatively long period of time of the wash cycle. Indeed, we found that it is possible to act against the decrease of the activity level of said peroxidase during the wash cycle. This is achieved in the present invention by supplementing the inactivated peroxidase with new active peroxidase in the wash environment. The new active peroxidase is supplemented in such a manner that the activity level of the peroxidase in the wash environment remains substantially constant. "Substantially constant" is hereinafter understood to include possible deviations of less than 50%, preferably less than 30% from the effective activity level maintained substantially constant. Preferably, said effective activity level for dye transfer inhibition and/or bleaching of said peroxidase

is reached as soon as possible at the beginning of the wash cycle. The "beginning of the wash cycle" is hereinafter understood to be within the first 5 minutes from the start of the wash cycle.

A possible way to achieve a substantially constant activity level of said peroxidase in said wash environment is to incorporate said peroxidase in a release agent. Said release agent is an agent which releases the incorporated peroxidase into the wash environment in a controlled manner. According to the present invention, the controlled introduction of peroxidase is such to keep a substantially constant level of active peroxidase in the wash environment.

A preferred embodiment of the present invention is a release agent being a combination of a fast release agent and a slow release agent. "Fast" is meant to be a relative measure with respect to "slow". Indeed, in the following it is understood that the fast release agent releases its incorporated peroxidase in the wash environment before the slow release agent. This means that the peroxidase incorporated in said fast release agent is available in the wash environment before the peroxidase incorporated into said slow release agent. Therefore, it is the slow release agent which supplements the wash environment with new peroxidase keeping the activity level of said peroxidase substantially constant.

For example, a fast release agent may be such that the maximum activity level of said peroxidase is reached in the beginning of the wash cycle. This means that the complete amount of peroxidase incorporated into said fast release agent is released in the beginning of the wash cycle. Preferably, the maximum activity level of said peroxidase may be reached within the first 5 minutes from the start of the wash cycle. The peroxidase released from said fast release agent is hereinafter called "first peroxidase". On the contrary, "second peroxidase" is intended to be the peroxidase released from said slow release agent.

We found that the activity level of the first peroxidase begins to decrease right after its complete release. For example, in certain wash environment conditions, we found that the activity level of said first peroxidase begins to decrease after about 5 minutes. To keep the activity level of the peroxidase in the wash environment constant, the second peroxidase may begin to be released when the activity of said first

peroxidase begins to decrease, such to supplement the inactivated first peroxidase. For example, in our standard wash environment as used before, said second peroxidase may begin to be substantially released at about 5 minutes, and the maximum activity level of said second peroxidase may be reached after about 20 minutes from the start of the wash cycle. For example, the peroxidase incorporated into the slow release agent as described in PCT/DK95/00214, as discussed above, may be used for the purpose of the present invention. In this example, the activity level of peroxidase in the wash environment may be kept substantially constant between about 5 minutes and 20 minutes from the start of the wash cycle. To further prolong the substantial constant activity level of peroxidase in the wash environment, said cleaning composition may further comprise peroxidase incorporated in an even slower release agent which supplements the inactivated second peroxidase.

Optionally, the substantial constant activity level of peroxidase may be kept constant during the whole duration of the wash cycle by having peroxidase incorporated in slower and slower release agents. Another option may be to have peroxidase made available in the wash environment only after a certain time from the start of the wash cycle. For example, said peroxidase may be incorporated in a slow release agent, which may be defined now as "fast release agent", and in a very slow release agent, which may be defined now as "slow release agent". The result of a substantially constant activity level, even if reached later in the wash cycle, is the same as discussed before. Preferably, the substantially constant activity level of peroxidase in the wash cycle is between about 0.01 to about 500 mg active peroxidase protein per liter of the wash solution, preferably about 0.1 to about 200 mg active peroxidase protein per liter of the wash solution. Preferably, the weight ratio between said peroxidase being incorporated into a fast release agent and said peroxidase being incorporated into a slow release agent is between 1:0.5 and 1:4

We found that the amount of enhancer and of the source of hydrogen peroxide can be reduced in said cleaning composition when the activity level of said peroxidase is kept substantially constant according to the present invention without losing any benefits of said peroxidase as a dye transfer inhibiting agent and/or as a bleaching agent. Instead, surprisingly,

we found that the dye transfer inhibition and/or the bleaching effect is significantly improved compared to a cleaning composition which does not keep the activity level of said peroxidase substantially constant during the wash cycle. Furthermore, we found that the reduced level of enhancer and of said source of hydrogen peroxide leads to a superior maintenance of sensitive dyes of fabrics. Sensitive dyes of fabrics may be, for example, the colour of the fabric itself which needs to be preserved as intact as possible on the fabric.

We found that a cleaning composition according to the present invention being mainly an enzymatic dye transfer inhibiting system may comprise an dye transfer inhibiting effective amount of enhancer and of source of hydrogen peroxide. As said before, said dye transfer inhibiting effective amount of enhancer and of source of hydrogen peroxide can be reduced when the activity level of said peroxidase is kept substantially constant. Said dye transfer inhibiting effective amount of enhancer and of source of hydrogen peroxide depends from the specific enhancer and source of hydrogen peroxide respectively used in said cleaning composition. For example, if the enhancer is 10-propionic acid phenothiazine, the dye transfer inhibiting effective amount of this enhancer in the wash liquor is preferably less than about 10 mMole per liter of wash solution, more preferably about 4 mMole per liter of wash solution. Furthermore, if the source of hydrogen peroxide is sodium percarbonate, the preferred dye transfer inhibiting effective amount of sodium percarbonate is less than about 50 ppm, more preferably about 35 ppm. This level of enhancer and of a source of hydrogen peroxide may be used, for example, in a detergent for coloured fabrics, for which dye transfer inhibition and maintenance of colour is important.

On the contrary, we found that a cleaning composition according to the present invention being mainly an enzymatic bleach system may comprise an bleach effective amount of enhancer and of source of hydrogen peroxide. As said before, said bleach effective amount of enhancer and of source of hydrogen peroxide can be reduced when the activity level of said peroxidase is kept substantially constant. Said bleach effective amount of enhancer and of source of hydrogen peroxide depends from the specific peroxidase, enhancer and source of hydrogen peroxide used in said

cleaning composition. For example, if the peroxidase is Coprinus Peroxidase, the enhancer is 10-propionic acid phenothiazine, the bleach effective amount of this enhancer in the wash liquor is preferably between about 10 and about 150 mMole per liter, more preferably between about 50 and 130 mMole per liter. Furthermore, if the peroxidase is still Coprinus Peroxidase and the source of hydrogen peroxide is sodium percarbonate, the preferred bleach effective amount of sodium percarbonate is more than 50 ppm, more preferably about 100 ppm. In general, the bleach effective amount is higher than the corresponding dye transfer inhibiting effective amount when the same type of peroxidase, enhancer and source of hydrogen peroxide are used. This level of enhancer and of a source of hydrogen peroxide may be used, for example, in a detergent for white fabrics, for which bleaching is important.

Preferably, said enhancer and/or said source of hydrogen peroxide may be also incorporated independently into a release agent according to the present invention. In this case, said enhancer and/or said source of hydrogen peroxide may be preferably incorporated independently in said fast and/or slow release agent. More preferably, said peroxidase and said enhancer may be incorporated together into a release agent according to the present invention, and said source of hydrogen peroxide may be incorporated independently into another release agent according to the present invention. In this manner, said enhancer and/or said source of hydrogen peroxide, being incorporated into a release agent, are also protected in the wash environment for a certain period of time. This allows to replace in the wash environment deactivated enhancers and/or sources of hydrogen peroxide in the same manner as for the peroxidase explained above. Consequently, the level of active enhancer and/or of source of hydrogen peroxide may be also maintained at a substantially constant level during a certain period of the wash cycle.

Preferably, said peroxidase is in the form of peroxidase-containing granules (in the following sometimes denoted as "peroxidase granulate" or as "peroxidase-containing granulate"). Said peroxidase granulate may suitably further contain various granulation aids, binders, fillers, lubricants and the like. Examples hereof include cellulose (e.g. cellulose in fibre or microcrystalline form), dextrans (e.g. yellow dextrin), polyvinylpyrrolidone,

polyvinylalcohol, cellulose derivatives (such as CMC or hydroxypropylcellulose), gelatin, salts (e.g. sodium sulfate, sodium chloride, calcium sulfate or calcium carbonate), titanium dioxide, talc and clays (e.g. kaolin or bentonite). Other materials of relevance for incorporation in the granulates of the type in question are described, for example, in EP 0 304 331 B1, and will be well known to persons skilled in the art. Said enhancer and said source of hydrogen peroxide may be also in the form of granulates. As a preferred option, when said enhancer is incorporated into a release agent, said peroxidase and said enhancer are granulated together forming a co-granulate to be incorporated into a release agent. Otherwise, independent enhancer-granulates and (source of hydrogen peroxide)-granulates may be also considered in the cleaning composition according to the present invention.

Methods and apparatus for producing enzyme-containing granulates are likewise well known to the skilled person (see, e.g. EP 0304 331 B1). Compact granulates - produced, e.g., using apparatus comprising knives as described in Example 1 in US Patent No. 4,106,991 - constitute very suitable granulates (co-granulates) in the context of the present invention.

The release agent may be, for example, a coating. Said coating protects said granulates (co-granulates) in the wash environment for a certain period of time. The coating will normally be applied to said granulates (co-granulates) in an amount in the range of 0% to 50% by weight (calculated on the basis of the weight of the uncoated, dry granulate), preferably in the range of 5 % to 40 % by weight. The amount of coating to be applied to said granulates will depend to a considerable extent on the nature and composition of the desired coating, and to the kind of protection said coating should offer to said granulates. For example, the thickness of said coating or a multi-layered coating applied onto any of the above granulates may determine the period in which the content of said granulates is released. A possible multi-layered coating may be a coating in which, for example, a fast release coating is coated over a slow release coating.

Suitable fast release or slow release coatings are coatings which give rise to fast or slow release of the contents of the peroxidase- and/or enhancer (co-granulates) and/or (source of hydrogen peroxide)-granulates

according to the present invention under the conditions prevailing during the use thereof. Thus, for example, when a preparation of the invention is to be introduced into a washing liquor containing a washing detergent (normally comprising, e.g. one or more types of surfactants), the coating should be one which ensures fast or slow release of the contents of said granulates from the release agent when it is introduced into the washing medium. A possible fast release agent may be, for example, an uncoated granulate.

Preferred fast or slow release coating are coatings which are substantially insoluble in water. Fast or slow release coatings which are appropriate in the context of dye-transfer inhibition and/or bleaching effect in washing media may suitably comprise substances selected from the following: tallow; hydrogenated tallow; partially hydrolyzed tallow; fatty acids and fatty alcohols of natural and synthetic origin; long-chain fatty acid mono-, di- and triesters of glycerol (e.g. glycerol monostearate); ethoxylated fatty alcohols; latexes; hydrocarbons of melting point in the range of 50-80°C; and waxes. Melt-coating agents are a preferred class of fast or slow release coating agents which can be used without dilution with water. Reference may be made to Controlled Release Systems : Fabrication Technology, Vol. I, CRC Press, 1988, for further information on slow release coating.

Coatings in general, including fast or slow release coatings, may suitably further comprise substances such as clays (e.g. kaolin), titanium dioxide, pigments, salts (such as calcium carbonate) and the like. The person skilled in the art will be aware of further coating constituents of relevance in the present invention.

In the following, Example 1 describes the preparation of a peroxidase-granulate incorporated into a fast and a slow release agent. Example 2 describes the preparation of a peroxidase-enhancer co-granulate into a fast and a slow release agent.

EXAMPLE 1

Granulation

2.0 kg of cellulose fibres (Arbocel TM BC 200), 0.9 kg of kaolin, 1.2 kg of yellow dextrin (TACKIDEX TM G155) and 10.1 kg of sodium sulfate (all dry components) were mixed in a Lödige mixer.

The above mixed dry components were sprayed, with continuous mixing, with 2.1 kg of liquid peroxidase concentrate (71 mg enzyme protein/g; Coprinus peroxidase produced as described in Example 1 in EP 505 311) to which had been added (and dissolved) 0.5 kg of sucrose and 0.8 kg of water.

During and after spraying, a compact peroxidase-granulate was formed by means of the knives described in Example 1 in US Patent No. 4,106,991.

When the granulation was finished, the peroxidase-granulate was dried on a fluidized bed. The dry peroxidase-granulate was sieved, and the product fraction of size between 300 and 1000 mm was separated for coating.

Coating

A peroxidase-granulate incorporated into a fast release agent is, for example, an uncoated peroxidase-granulate. A peroxidase-granulate incorporated into a slow release agent may be made in the following manner. The peroxidase-granulate to be incorporated into a slow release agent was heated to 60°C in a Lödige mixer, and 5% of glycerol monostearate (also heated to 60°C) was added under continuous mixing. When the glycerol monostearate was distributed, the peroxidase-granulate was powdered with 6.7% of organoclay (Claytone TM AF) and 6.7% of titanium dioxide under continuous mixing. All percentages are weight percentages relative to the dry uncoated peroxidase-granulate. After cooling, the coated peroxidase-granulate, i.e. the peroxidase-granulate incorporated into slow release agent, was sieved and the fraction in the size range 300-1100 mm was collected for use.

EXAMPLE 2

Granulation

5.2 kg of cellulose fibres (Arcobel TM BC200), 4.2 kg of enhancer (PPT), 2.4 kg of kaolin, 1.2 kg of yellow dextrin (TACKIDEX TM G155) and 23.1 kg of sodium sulfate (all dry components) were mixed in a Lödige mixer FM-F 130.

The above mixed dry components were sprayed, with continuous mixing, with 2.3 kg of liquid peroxidase concentrate (56.7 mg enzyme protein/g; Coprinus peroxidase produced as described in Example 1 in EP 505 311) in which had been dissolved 3.6 kg of sucrose.

During and after spraying, a compact peroxidase-enhancer co-granulate was formed by means of the knives described in Example 1 in US Patent No. 4,106,991.

When the granulation was finished, the peroxidase-enhancer co-granulate was dried on a fluidized bed. The dry granulate was sieved, and the product fraction of size between 300 and 1000 μ m was separated for coating.

Coating

Again, a peroxidase-enhancer co-granulate incorporated into a fast release agent is, for example, an uncoated peroxidase-enhancer co-granulate. A peroxidase-enhancer co-granulate incorporated into a slow release agent may be made in the following manner. The peroxidase-enhancer co-granulate was heated to 60°C in a Lödige FM 50 mixer, and 3% of melted hydrogenated tallow (also heated to 60°C) was added under continuous mixing. When the tallow was distributed, the peroxidase-enhancer co-granulate was powdered with 3.5% of kaolin and 3.5% of titanium dioxide under continuous mixing. 3% of glycerol monostearate (heated to 60°C) was then added under continuous mixing. When the glycerol monostearate was distributed, the peroxidase-enhancer co-granulate was powdered with 1.5% of kaolin with mixing. All percentages are weight percentages relative to the dry uncoated granulate. After cooling, the coated

peroxidase-enhancer co-granulate was sieved and the fraction in the size range 300-1100 μ m was collected for use.

Further components of said cleaning composition

Said cleaning composition according to the present invention may preferably be used in laundry detergent compositions, in dish detergent compositions and in fabric softening compositions. Said cleaning composition may be also used as an additive in the laundry or dish washing. Nevertheless, other possible applications are in health care products, e.g. disinfectants, and beauty care products, e.g. hair treatment or colouring.

The pH of said cleaning composition (measured in aqueous solution at use concentration) depends from the specific type of said cleaning composition. For example, laundry detergent compositions usually have a neutral or alkaline pH, e.g. a pH in the range of about 7 to 11. On the contrary, additives, when used without any other detergent, usually have an acidic or neutral-alkaline pH, e.g. a pH in the range of about 4 to about 8. Said cleaning composition according to the invention may be in any convenient form, e.g. in the form of solid, tablet, powder, granules, paste or liquid.

Enzymes

Preferred cleaning compositions, in addition to peroxidase of the present invention, comprise other enzyme(s) which provides cleaning performance and/or fabric care benefits. Such enzymes include protease, lipase, amylase, cellulase, cutinase, or an oxidase.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Nordisk A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and

Optimase by Solvay Enzymes. Also proteases described in application USSN 08/136,797 can be included in the cleaning composition of the invention. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Other preferred enzymes that can be included in the cleaning compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R (Novo) which have found to be very effective when used in combination with the compositions of the present invention.

The lipases are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of active enzyme by weight of the cleaning composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl^R (Novo Nordisk), Fungamyl^R and BAN^R (Novo Nordisk).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Said cellulases is normally incorporated in the cleaning composition at levels from 0.0001% to 2% of active enzyme by weight of the cleaning composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Said enzymes are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of active enzyme by weight of the cleaning composition. Mixture in the above enzymes are encompassed herein, in particular mixtures of a protease, an amylase, a lipase and/or a cellulase.

Enzymes (e.g. proteases) incorporated in the cleaning composition according to the invention may be stabilized by means of conventional stabilising agents, e.g. a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, a boric acid derivative such as, e.g. an aromatic borate ester, or an organoboronic or -borinic acid, and the cleaning according to the invention may be formulated as described in, e.g., WO 92/19709 and WO 92/19708.

Where appropriate, enzymes may be incorporated in the cleaning composition in the form of, e.g., a non-dusting granulate or a protected enzyme. Non-dusting granulates may be produced, e.g., as disclosed in US 4,106,991 and 4,661,452 (both to Novo Industri A/S) and may optionally be coated by methods known in the art. Examples of waxy coating materials are poly(ethylene oxide) products (polyethyleneglycol, PEG) with mean molecular weights of 1000 to 20000. Examples of film forming coating materials suitable for application by fluid bed techniques

are given in patent GB 1483591. Protected enzymes may be prepared according to the method disclosed in EP 0 238 216.

Surfactant system

The cleaning compositions according to the present invention comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants. The surfactant is typically present at a level of from 0.1% to 60% by weight.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Preferred non-alkylbenzene sulfonate surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

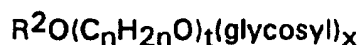
The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use

as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O5O (the condensation product of C₁₂-C₁₄ alcohol with 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic

group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



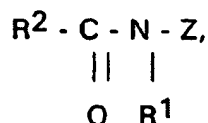
wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula



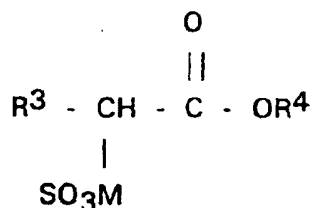
wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula

$RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - $C_{18}E(2.25)M$), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - $C_{18}E(3.0)M$), and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - $C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8 - C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein R^3 is a C_8 - C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1 - C_6 hydrocarbyl, preferably an alkyl, or combination

thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the laundry cleaning compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and

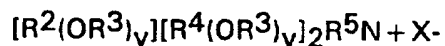
unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_k-CH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry cleaning compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

The laundry cleaning compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the laundry cleaning compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining

the two R^4 groups, $-\text{CH}_2\text{CHOH}-\text{CHOHCOR}^6\text{CHOHCH}_2\text{OH}$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R_1 is C_8 - C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl.

The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis.

Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- coconut trimethyl ammonium chloride or bromide;
- coconut methyl dihydroxyethyl ammonium chloride or bromide;
- decyl triethyl ammonium chloride;
- decyl dimethyl hydroxyethyl ammonium chloride or bromide;
- C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
- coconut dimethyl hydroxyethyl ammonium chloride or bromide;
- myristyl trimethyl ammonium methyl sulphate;
- lauryl dimethyl benzyl ammonium chloride or bromide;
- lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
- choline esters (compounds of formula (i) wherein R_1 is $\text{CH}_2\text{-CH}_2\text{-O-C-C}_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).



di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

When included therein, the laundry cleaning compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the laundry cleaning compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

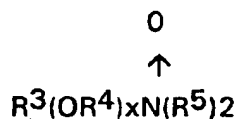
When included therein, the laundry cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the laundry cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably

from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopenta-dienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacar-boxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the cleaning compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_4EDDS . Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition. Preferred levels of builder for liquid cleaning compositions are from 5% to 30%.

Optional detergent ingredients

Additional optional detergent ingredients that can be included in the cleaning compositions of the present invention include bleaching agents such as PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 0.1% to about 10%. In general, bleaching compounds are optional added components in non-liquid formulations, e.g. granular detergents.

The bleaching agent component for use herein can be any of the bleaching agents useful for cleaning compositions including oxygen bleaches as well as others known in the art.

The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy-caproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. In addition, very suitable are the bleach activators C8(6-octanamido-caproyl)oxybenzenesulfonate, C9(6-nonanamido caproyl)oxybenzenesulfonate and C10(6-decanamido caproyl)oxybenzenesulfonate or mixtures thereof. Also suitable activators are acylated citrate esters such as disclosed in European Patent Application No. 91870207.7.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in cleaning compositions according to the invention are described in application USSN 08/136,626.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, cleaning compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent

Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in European Patent application N°92201649.8. Said compositions can comprise a silicone/ silica mixture in combination with fumed nonporous silica such as Aerosil^R.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Other components used in cleaning compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes. Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

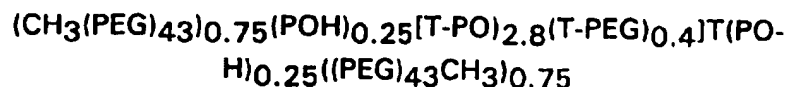
Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-tri-azin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US

Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pcOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

Softening agents

Fabric softening agents can also be incorporated into laundry cleaning compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-

B-O 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-O 299 575 and O 313 146.

Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Polymeric dye transfer inhibiting agents

The cleaning compositions according to the present invention may also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into cleaning compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof. Addition of such polymers also enhances the performance of the enzymes according the invention.

The cleaning compositions according to the invention can be in liquid, paste, gels, bars or granular forms. Granular compositions according to the

present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular cleaning compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid cleaning compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the cleaning compositions.

The compositions of the invention may for example, be formulated as hand and machine laundry cleaning compositions including laundry additive compositions and compositions suitable for use in the pretreatment of stained fabrics, rinse added fabric softener compositions, and compositions for use in general household hard surface cleaning operations and dishwashing operations.

The peroxidase, enhancer and source of hydrogen peroxide according to the present invention may be added in the following examples of cleaning compositions. The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

The amount of the components in all the exemplified cleaning compositions are expressed in % of weight of the cleaning composition. In the cleaning compositions, the abbreviated component identifications have the following meanings:

PES	: Peroxidase-enhancer-source of hydrogen peroxide system according to the present invention
LAS	: Sodium linear C ₁₂ alkyl benzene sulphonate
TAS	: Sodium tallow alkyl sulphate
XYAS	: Sodium C _{1X} - C _{1Y} alkyl sulfate
SS	: Secondary soap surfactant of formula 2-butyl octanoic acid
25EY	: A C ₁₂ -C ₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
45EY	: A C ₁₄ - C ₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEZX	: C _{1X} - C _{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
Nonionic	: C ₁₃ -C ₁₅ mixed ethoxylated/ propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafax LF404 by BASF GmbH
CFAA	: C ₁₂ -C ₁₄ alkyl N-methyl glucamide
TFAA	: C ₁₆ -C ₁₈ alkyl N-methyl glucamide
Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio = 2.0)
NaSKS-6	: Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
Carbonate	: Anhydrous sodium carbonate

Phosphate	: Sodium tripolyphosphate
MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Polyacrylate	: Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
Zeolite A	: Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 1 to 10 micrometers
Citrate	: Tri-sodium citrate dihydrate
Citric	: Citric Acid
Perborate	: Anhydrous sodium perborate monohydrate bleach, empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
PB4	: Anhydrous sodium perborate tetrahydrate
Percarbonate	: Anhydrous sodium percarbonate bleach of empirical formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
BAct	: Bleach activator, like tetraacetyl ethylene diamine (TAED) or nonanoyloxybenzene sulfonate (NOBS)
Protease	: Proteolytic enzyme sold under the tradename Savinase by Novo Nordisk A/S
Amylase	: Amylolytic enzyme sold under the tradename Termamyl by Novo Nordisk A/S
Lipase	: Lipolytic enzyme sold under the tradename Lipolase by Novo Nordisk A/S
Cellulase	: Cellulosic enzyme sold under the tradename Carezyme or Celluzyme by Novo Nordisk A/S
CMC	: Sodium carboxymethyl cellulose

DETPMP	: Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
PVP	: Polyvinyl pyrrolidone polymer
EDDS	: Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt
Suds Suppressor	: 25% paraffin wax Mpt 50°C, 17% hydrophobic silica, 58% paraffin oil
Granular Suds Suppressor	: 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form
Sulphate	: Anhydrous sodium sulphate
HMWPEO	: High molecular weight polyethylene oxide
TAE 25	: Tallow alcohol ethoxylate (25)

Example 3

A granular fabric cleaning composition in accordance with the invention was prepared as follows :

Sodium linear C12 alkyl benzene sulfonate	6.5
Sodium sulfate	15.0
Zeolite A	26.0
Sodium nitrilotriacetate	5.0
Enzyme	0.02
PVP	0.5
Boric acid	4.0
PES, BAct and minors	up to 100%

Example 4

A compact granular fabric cleaning composition (density 800g/l) in accord with the invention was prepared as follows:

45AS	8.0
25E3S	2.0
25E5	3.0
25E3	3.0
TFAA	2.5
Zeolite A	17.0
NaSKS-6	12.0
Citric acid	3.0
Carbonate	7.0
MA/AA	5.0
CMC	0.4
Protease	0.05
Lipase	0.005
Cellulase	0.001
Amylase	0.01
EDDS	0.3
Granular suds suppressor	3.5
PES, BAct water and minors	up to 100%

Example 5

Granular fabric cleaning compositions in accordance with the invention which are especially useful in the laundering of coloured fabrics were prepared as follows :

	I	II
LAS	10.7	-
TAS	2.4	-
TFAA	-	4.0
45AS	3.1	10.0
45E7	4.0	-
25E3S	-	3.0
68E11	1.8	-
25E5	-	8.0
Citrate	15.0	7.0
Carbonate	-	10
Citric acid	2.5	3.0
Zeolite A	32.1	25.0
Na-SKS-6	-	9.0
MA/AA	5.0	5.0
DETPMP	0.2	0.8
Protease	0.02	0.01
Lipase	0.04	0.005
Amylase	0.03	0.005
Cellulase	-	0.001
Silicate	2.5	-
Sulphate	5.2	3.0
PVP	0.5	-
Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone	-	0.2
PES, water and minors	up to 100%	

Example 6

Granular fabric cleaning compositions in accordance with the invention which provide "softening through the wash" capability were prepared as follows:

	I	II
45AS	-	10.0
LAS	7.6	-
68AS	1.3	-
45E7	4.0	-
25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.02	0.001
Pectinase	0.01	0.02
Silicate	3.0	5.0
Carbonate	10.0	10.0
Granular suds suppressor	1.0	4.0
CMC	0.2	0.1
PES, BAct, water and minors	up to 100%	

Example 7

Heavy duty liquid fabric cleaning compositions in accordance with the invention were prepared as follows:

	I	II
LAS acid form	-	25.0
Citric acid	5.0	2.0
25AS acid form	8.0	-
25AE2S acid form	3.0	-
25AE7	8.0	-
CFAA	5	-
DETPMP	1.0	1.0
Fatty acid	8	-
Oleic acid	-	1.0
Ethanol	4.0	6.0
Propanediol	2.0	6.0
Protease	0.02	0.02
Amylase	0.01	0.005
Cellulase	0.01	0.01
Coco-alkyl dimethyl hydroxy ethyl ammonium chloride	-	3.0
Smectite clay	-	5.0
PVP	2.0	-
PES, water and minors	up to 100%	

An enzymatic dye transfer inhibiting system and enzymatic bleach system according to the present invention are exemplified in the following Examples.

Example 8

An enzymatic dye transfer inhibiting system according to the present invention, comprising the peroxidase enzyme in coated granulates, a bleach enhancer and a hydrogen peroxide source, is incorporated in a typical colour detergent matrix as described, for example, in composition of Example 5 above and with solution having a pH of between about 8.5 and

about 9.8. The pH of the solution is trimmed with citric acid to the desired value.

The peroxidase enzyme is present in two different granulates which release the peroxidase sequentially with different release rates in a wash solution at 40°C. The first granulate has a fast release of the peroxidase delivering 70 micro gram peroxidase active protein per liter of wash liquor, averaged versus time. The second peroxidase granulate is coated according to the description in Example 1 above and has a slower peroxidase release profile delivering 165 micro gram peroxidase active protein per liter wash liquor, averaged versus time. The combined release profiles of the two peroxidase granulates maintain a substantially constant peroxidase level in the wash.

The dye transfer inhibiting bleach enhancer is a substituted phenothiazine and is added via another granulate with a fast release profile. Preferred enhancer and level in the wash liquor is 10-propionic acid phenothiazine at 4 mMole.

The hydrogen peroxide source is Sodium perborate mono hydrate or Sodium percarbonate at 35 ppm in the wash liquor.

Performance of the enzymatic dye transfer inhibiting system:

In laundry performance tests the above system delivers superior dye transfer inhibiting effect on dyes bleeding in solution from collared fabrics during the wash when compared to the nil-[enzymatic dye transfer inhibiting]-system containing detergent.

The dye transfer inhibiting performance of the above system with controlled peroxidase release and with the very low level of bleach enhancer is equivalent to same system with 5-fold level of bleach enhancer (20 mMole) but with one single addition of fast releasing peroxidase (200 mggram peroxidase active protein per liter). Also a high whitening effect and colour maintenance has been found due to the dye-transfer-inhibition of bleeding dyes in solution. In addition the enzymatic bleach systems has a sanitation effect on the laundered fabrics.

Example 9

An enzymatic bleach system according to the present invention, comprising the peroxidase enzyme in coated granulates, a bleach enhancer and a hydrogen peroxide source, is incorporated in a typical colour detergent matrix as described, for example, in composition of Example 5 above.

The peroxidase enzyme is present in up to 3 different granulates which release the peroxidase sequentially in order to maintain a substantially constant peroxidase level of about 60 to about 200 mg/ml active peroxidase protein per liter of the wash solution and during the whole main wash process of 35 to 60 minutes at 40°C. The first granulate has a fast release of the peroxidase and the two others have a slower peroxidase release profiles.

The bleach enhancer is a substituted phenothiazine or phenoxazine and is added via other granulate with fast release profile. Preferred enhancers and level in the wash are 10-propionic acid phenothiazine at about 50 to about 130 mMole, 10-methyl phenothiazine at about 150 to about 250 mMole; 10-ethyl 4-carboxylic acid phenothiazine at about 100 to about 250 mMole.

The hydrogen peroxide source is Sodium perborate mono hydrate or Sodium percarbonate at 100 ppm in the wash liquor.

Performance of the enzymatic bleach system:

In laundry performance tests the above system delivers significant bleach performance versus the single addition of the fast released peroxidase in the wash and when compared to the nil-[enzymatic bleach]-system containing detergent.

The enzymatic bleach system according to the present invention delivers superior bleaching of stains based on beta-carotene and lycopene e.g. in tomato sauce, spaghetti sauce, on stains based on flavonoid pigments e.g. anthocyanin and antoxanthine based colorant in many fruit stains like in black berry; mango, pomme granate and on polyphenolic staining materials as in wine, coffee and tea.

Furthermore, the enzymatic bleach system according to the invention delivers significant cleaning benefits on realistically soiled items e.g. on stained tea-towel, underwear, collar and cuffs of shirts and socks. Also a high whitening effect and colour maintenance has been found due to the significant dye-transfer-inhibition of bleeding dyes in solution. In addition the enzymatic bleach systems has a sanitation effect on the laundered fabrics.

Other advantage of the enzymatic bleach systems as described in the invention is the weight efficiency versus the activated bleach system with high level of hydrogen peroxide in current detergents. The enzymatic bleach system takes up to 5 % in the detergent composition versus 20 to 25 % for TAED activated bleach system in a typical compact detergent as described, for example, in compositions of Examples 3 and 4 above. This makes the enzymatic bleach system suitable for developing further compacted granular detergents.

Example 10

A laundry bleach-additive containing the enzymatic bleach system according to the present invention comprises the peroxidase granulates with different release agents according to example 1 and the bleach enhancer in powder form. The preferred enhancer is 10-propionic acid phenothiazine. The hydrogen peroxide is delivered via enzymatic system (example B; glucose oxidase / glucose) or via the sodium perborate or sodium percarbonate (example A).

The additive contains a buffer controlling the wash solution pH in the range between about 5 to about 7.5 when used without any detergent. Non-ionic detergent is added for improved wetting of the laundered fabrics when the additive is used as such without detergent. Optional ingredients are perfumes, suds controller and process aids. The additive can be executed as a powder or as liquid or can be in fast dissolving tablet form. The additive can be used as such e.g. in a hand wash application or in a laundry process in the pre-wash step or in combination with nil-bleach granular or liquid detergents in the main wash. The additive provides the

performance benefits as described in example 8 and 9 when used at concentrations of between about 3 to about 7 g/L of wash solution.

Ingredients	A	B
	%	%
Peroxidase granulate fast release (9.5 mg prot. /g)	0.2	0.2
Peroxidase granulate slow release (7.8 mg prot./g)	0.8	0.8
Enhancer powder 95%	0.75	0.75
Sodium percarbonate/perborate mono hydrate	2.2	-
Glucose oxidase (2000 Glucose oxidase Units/g)	-	0.2
Glucose mono hydrate	-	30
Sodium citrate/Citric acid to solution pH 5-7	65	60
Non-ionic surfactant (low foaming)	1-5	1-5
Minors	balance to100	balance to100

Claims :

1. A cleaning composition comprising peroxidase, an enhancer and a source of hydrogen peroxide, said peroxidase being incorporated into a release agent, characterized in that said release agent is such that the level of active peroxidase is substantially held constant in the wash environment during a substantial period of the wash cycle.
2. A cleaning composition according to claim 1 characterized in that said peroxidase is incorporated into a fast release agent and a slow release agent.
3. A cleaning composition according to any of the preceding claims characterized in that the weight ratio between said peroxidase being incorporated into a fast release agent and said peroxidase being incorporated into a slow release agent is between 1:0.5 and 1:4.
4. A cleaning composition according to any of the preceding claims characterized in that said enhancer is incorporated independently from said peroxidase into a release agent.
5. A cleaning composition according to claims 1-3 characterized in that said enhancer is incorporated together with said peroxidase into a release agent.
6. A cleaning composition according to any of the preceding claims characterized in that said source of hydrogen peroxide is incorporated independently into said release agent.
7. A cleaning composition according to any of the preceding claims characterized in that said enhancer is present in said cleaning composition in a dye transfer inhibiting effective amount.
8. A cleaning composition according to claim 7 characterized in that said source of hydrogen peroxide is present in said cleaning composition in a dye transfer inhibiting effective amount.

9. A cleaning composition according to any of claims 7 and 8 characterized in that said cleaning composition is a enzymatic dye transfer inhibiting system.
10. A cleaning composition according to any of the claims 1 to 6 characterized in that said enhancer is present in said cleaning composition in a bleach effective amount.
11. A cleaning composition according to claim 10 characterized in that said source of hydrogen peroxide is present in said cleaning composition in a bleach effective amount.
12. A cleaning composition according to any of claims 10 and 11 characterized in that said cleaning composition is a enzymatic bleach system.
13. A cleaning composition according to any of the preceding claims characterized in that said cleaning composition is a liquid or a granular cleaning composition.

INTERNATIONAL SEARCH REPORT

Internat. J. Application No
PCT/US 96/02229

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 451 337 (LIU DON K. K. ET AL.) 19 September 1995 see column 2, line 35 - column 5, line 58 see column 6, line 9 - line 28 see claims ---	1,7-13
X	WO,A,95 33039 (NOVO NORDISK A/S) 7 December 1995 cited in the application see page 2, line 15 - page 9, line 14 see claims 1-5 ---	1,5,7-13
X	WO,A,95 10602 (NOVO NORDISK A/S) 20 April 1995 cited in the application see page 12, line 10 - line 35 see page 13, line 9 - page 15, line 3 see claims 1,5-12 --- -/--	1,7-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

4 October 1996

Date of mailing of the international search report

21. 10. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Serbetsoglou, A

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 96/02229

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,94 12619 (NOVO NORDISK A/S) 9 June 1994 cited in the application see page 9, line 8 - page 10, line 1 see claims 1-18 ---	1,7-13
A	US,A,4 106 991 (MARKUSSEN ERIK KJAER ET AL) 15 August 1978 cited in the application see claims 1,9-11 ---	1
A	GB,A,2 233 653 (THE BRITISH PETROLEUM CO.) 16 January 1991 see page 2 see claims 1,4-7 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/02229

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5451337	19-09-95	AU-A- 2294095 WO-A- 9533040	21-12-95 07-12-95
WO-A-9533039	07-12-95	AU-A- 2560895	21-12-95
WO-A-9510602	20-04-95	AU-A- 7853194 EP-A- 0724631 FI-A- 961650	04-05-95 07-08-96 15-04-96
WO-A-9412619	09-06-94	CA-A- 2150564 EP-A- 0672125 FI-A- 952646 JP-T- 8503370	09-06-94 20-09-95 31-05-95 16-04-96
US-A-4106991	15-08-78	GB-A- 1590432 AU-B- 509934 AU-A- 2675377 BE-A- 856536 CA-A- 1094000 CH-A- 632788 DE-A- 2730481 FR-A- 2357301 JP-C- 1308499 JP-A- 53006484 JP-B- 58026315 NL-A- 7707517 SE-B- 425294 SE-A- 7707837	03-06-81 29-05-80 11-01-79 06-01-78 20-01-81 29-10-82 12-01-78 03-02-78 26-03-86 20-01-78 02-06-83 10-01-78 20-09-82 08-01-78
GB-A-2233653	16-01-91	NONE	

THIS PAGE BLANK (US 1)